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A11105 852012

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
S. W. STRATTON, Director

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS No. 105
[Issued December 10, 1917]

COMPARATIVE TESTS OF PORCELAIN LABORATORY WARE

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Porcelain is of but slightly less importance than glass in the chemical laboratory. In ordinary use it soon becomes evident whether or not the ware is mechanically strong and whether it is able to withstand sudden changes in temperature. In exact analytical work it is equally important that the glaze should offer the maximum resistance to attack by reagents. For many years chemists had at their disposal certain makes of ware which were of excellent quality, so that the resistance of porcelain to reagents was almost a laboratory byword. The placing on the market of ware from other sources and the inability to obtain the familiar brands made it desirable to subject both the new and old kinds to a series of comparative tests.

At the outset it was recognized that the results would probably not be as clear-cut and definite as those with glass. The weight of the porcelain prevented the testing of crucibles and dishes above a certain limited size. This meant that only a small surface of presumably highly resistant material would be exposed to attack. In addition, the shapes of the crucibles, and still more of the dishes, varied for the different makes, so that with a given volume of reagent not necessarily the same area of glaze would be attacked. During the progress of the work it was found that this factor was of slight importance, because the losses due to the action of the reagents were usually so small as to be negligible for most analytical work. After all it is desirable to know to what extent a given volume of solution may become contaminated, rather than how many square centimeters of porcelain it will wet.

BRANDS TESTED

At the time the tests were made only five makes of glazed porcelain ware could be obtained. In the laboratory stock the necessary number of Royal Berlin dishes, but no crucibles, was found. Meissen ware could not be obtained, but dishes and crucibles of "Bavarian" ware were purchased. In addition to these, a supply of a Japanese brand, marked "S. C. P.," and of two American makes, Herold (Coors) and Guernsey, were bought. All of the purchases were made in the open market.

The dishes were the largest that could be placed upon the balance pans. Nominally 80 mm in diameter, they varied from 78 to 95 mm for the different makes. The crucibles ranged in height from 35 to 50 mm, and in diameter from 57 to 65 mm. The different pieces of any one kind of ware were quite uniform in diameter and in general shape, but the variations in thickness were rather large. This was shown by the weights, which varied as follows: Herold (Coors), 34.5 to 43.1 g; Guernsey, 36.2 to 44.5 g; Bavarian, 34.1 to 43.0 g; Berlin, 29.4 to 37.3 g; Japanese, 32.3 to 43.0 g. The last-named ware showed the maximum variation, which amounted to 33 per cent. These figures are for 33 to 36 dishes of each kind of porcelain.

PREPARATION OF PIECES

Each piece was roughly weighed and, after having been arranged in the order of its weight, was lightly marked near the rim by means of a writing diamond. During the tests no breaks started at these diamond scratches. The lightest piece of each kind was used as a tare against which all weighings of that ware were made.

The pieces for the heating tests were not cleaned further than by wiping with a damp towel before the first rough weighing. The pieces used to test the action of reagents were rinsed with water, hydrochloric acid (1:1), and again with water, after which they were wiped dry on the outside. They were then kept filled with distilled water for 20 hours, rinsed, wiped dry, heated to 110° for two hours, cooled in the air, and weighed not sooner than three-fourths hour and usually much longer after their removal from the air bath. The tares were heated with the test pieces before each set of weighings.

SELECTION OF TEST METHODS

Suggestions as to the methods of testing and the reagents to use were received from various sources. No particular search of the literature was made, but it is believed that the fusions with sodium nitrate and the ignition with ferric oxide are new. The reasons for most of the tests are obvious, and for the others are given further on.

EXPERIMENTAL

All tests were made in duplicate, and the results are given in tabular form.

SUDDEN COOLING

Each piece was three-fifths filled with paraffin at 100° C, then brought to the desired temperature on a hot plate. It was then floated on water at room temperature. There were no failures on cooling from 200° C, but a number of dishes and crucibles cracked or broke when they were cooled from 225° C.

SUDDEN HEATING

The pieces were placed on a wire triangle and heated in the full flame of a Fletcher burner of the Méker type. After 3 minutes the flame was removed and 10 seconds later the piece was removed with platinum-tipped tongs. By this time the porcelain had cooled to a pale straw-yellow, at which temperature it would ordinarily be placed in a desiccator or otherwise handled with tongs. Quite unexpectedly this proved to be an important test, for in many cases the glaze cracked where touched by the tongs. When this happened after the first heating, new cracks were formed after one or more of the three succeeding heatings of 2 minutes each. In no case did the cracks first appear after one of these later heats.

The Royal Berlin and Japanese wares withstood this test satisfactorily.[1]

TREATMENT WITH SODIUM HYDROXIDE

After the usual preliminary cleansing, drying, and weighing, each piece was placed on the steam bath and then 50 cc of 10 per cent sodium-hydroxide solution was carefully poured in. The dishes did not rest in the openings of the bath but on thin plates of aluminum, in order to avoid the solvent action of directly impinging steam. After five hours' heating, 30 cc of water was added to each dish to make up for that lost by evaporation. An hour later the pieces were rinsed out under the tap, dipped into hydrochloric acid (1:1), again washed, wiped dry, heated in the air bath, and finally weighed after cooling in the air. A second treatment exactly like the first was given.

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[1] Samples of Coors ware of recent manufacture have been found to withstand this test.

The losses in weight found were greater than those caused by any other reagent, but the crucibles gave so much lower figures than the dishes that only the latter were used in the remaining solubility tests.

TREATMENT WITH SODIUM CARBONATE

The solution used contained 100 g of the anhydrous salt in 1,000 cc. The dishes were cleansed as for the preceding test. There were two treatments of seven hours each. The losses by evaporation were made up by adding 10-cc portions of distilled water at intervals of about two hours.

TREATMENT WITH SULPHURIC ACID

The cleansed and weighed dishes, each containing 25 cc of concentrated sulphuric acid, were heated on a hot plate for three hours at a temperature high enough to cause strong fuming. After washing out the acid and drying and weighing the dishes, it was noticed that one of them had a small crevice in the edge. Since this still contained acid, all the dishes were soaked in distilled water for three hours, rinsed, dried, and again weighed.

TREATMENT WITH FUSED SODIUM NITRATE

Since no oven suitable for use at temperatures above the melting point of sodium nitrate was available, the dishes were heated over burners. Thirty grams of the salt were placed in each dish and kept for two hours at such a temperature that there was a slight crust around the edges, while most of the nitrate was in the fused state. The melted salt was poured out and the cooled dishes were soaked for one and one-half hours in running water, then rinsed with dilute hydrochloric acid followed by distilled water. They were wiped dry, heated to 110° C, cooled, and weighed.

The losses in weight under this treatment were so unexpectedly small that a new series of tests was made with the same dishes at a higher temperature. The same weight of nitrate as before was slowly heated up to the point at which a piece of charcoal floating on it caught fire. This required about 10 minutes. Under this treatment there were further losses, but the figures in the table, which show the combined losses during the two fusions, were still small.

TREATMENT WITH FUSED SODIUM-NITRATE-CARBONATE MIXTURE

A mixture of 10 parts of sodium nitrate and 1 part of carbonate readily fuses to a clear melt at a temperature higher than the melting point of the nitrate alone, yet still below a red heat. The action of even this strongly alkaline reagent was slight when 33 g of it was kept just at the melting point for two hours. After the usual cleansing and weighing the dishes were soaked in distilled water overnight. The very small changes in weight thus resulting are evidence against any considerable porosity of the porcelain. The figures in the table give the total losses during the three fusions.

The glaze at the bottom of some of the dishes was dulled, but did not appear to have been badly attacked.

IGNITION WITH FERRIC OXIDE

Ferric oxide so readily stains porcelain and is often so hard to remove as to suggest that it forms a silicate with the glaze. In this case the removal of the stain by prolonged digestion with hydrochloric acid might be expected to remove silica in soluble form, and possibly also other constituents of the altered glaze.

In order to coat the dishes as uniformly as possible with ferric oxide before ignition, the following procedure was adopted: To 20 cc of a solution of ferric nitrate (equivalent to 57 mg of Fe_2O_3) was added 5 cc of ammonia of half strength. The whole was evaporated to dryness, first on the steam bath and then in a radiator.[2] This was followed by gentle ignition over a small flame and finally five minutes' heating in the full flame of a Fletcher burner. After cooling, the dishes were wiped as clean as possible and weighed. Although all were badly stained, their increase in weight due to adhering ferric oxide was in no case as much as 1 mg. To each dish there was added 40 cc of hydrochloric acid (1:1) which removed the stains by digesting on the steam bath for three-fourths hour. The dishes were soaked in running water for one hour, then cleaned, dried, and weighed. The losses in weight were all very small and gave no evidence of the formation of any considerable amount of soluble silicates.

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[2] Hillebrand, Bull. 422, U. S. Geol. Survey, p. 31, 1916.

POROSITY

The dishes that had been used in the nitrate fusions were soaked overnight in an aqueous solution of methyl violet, then rinsed quickly and wiped dry. All were strongly colored around the unglazed rim, and the numbers scratched on by the writing diamond stood out plainly. The spots where the glaze was dulled were faintly dyed. Nearly all of the color was removed by soaking for 20 hours in distilled water. In no case was there any evidence of pores or channels in the body of the material. The purple band around the edge was sharply limited by the glaze and showed no sign of creeping in under it. The dyeing effect seems to be due to adsorption by the rougher parts of the surface.

Results of Tests on Crucibles

Nature of test	Herold (Coors)		Guernsey		Bavarian		Japanese	
Heated to 200° C with paraffin and cooled suddenly in water	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Heated to 225° with paraffin and cooled as above	(b)	(c)	(c)	(b)	(c)	(c)	(b)	(b)
Suddenly heated in flame of Fletcher burner	(d)	(d)	(e)	(e)	(d)	(d)	(f)	(f)
Changes in weight in milligrams when—								
Heated with 10 per cent NaOH for 6 hours:								
First treatment	−1.8	− 1.9	−1.1	−1.6	−1.1	−1.6	−0.9	−0.7
Second treatment	−2.0	− 1.9	−1.7	−1.4	−1.2	−1.4	−0.7	+0.2

[a] The ware withstood this test satisfactorily.

[b] Did not crack.

[c] Cracked badly.

[d] Glaze cracked under tongs. Recent samples of Coors ware withstood this test.

[e] At third heat cracked badly at top and near bottom; glaze also cracked under tongs.

[f] No cracks in glaze.

Results of Tests on Dishes

Nature of test	Herold (Coors)		Guernsey		Bavarian		Royal Berlin		Japanese	
Heated to 200° C with paraffin and cooled suddenly in water.	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Heated to 125° C with paraffin and cooled as above	(b)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Suddenly heated in flame of Fletcher burner	(d)	(e)	(f)	(f)	(g)	(g)	(g)	(g)	(g)	(g)
Changes in weight in milligrams when—										
Heated with 10 per cent NaOH for 6 hours:										
First treatment	−2.3	−2.3	−2.6	−3.0	−2.5	−2.0	−1.4	−3.2	−1.0	−1.0
Second treatment	−2.6	−2.0	−2.5	−2.3	−2.4	−2.1	−0.6	−2.3	−1.2	−0.9
Heated with 10 per cent Na_2CO_3 for 7 hours:										
First treatment	−0.1	−0.1	+0.2	+0.1	−0.3	−0.3	−0.1	0.0	+0.3	+0.2
Second treatment	−0.3	−0.1	−0.8	−0.1	−0.3	−0.2	−0.1	−0.2	−0.3	−0.4
Heated with concentrated H_2SO_4:										
After washing	−0.1	0.0	−0.2	+0.1	0.0	−0.1	0.0	+0.1	0.0	0.0
After soaking (total)	−0.4	−0.4	−0.4	−0.3	−0.4	−0.5	+0.2	−0.3	−0.3	−0.4
Heated with fused $NaNO_3$ for 2 hours	0.0	+0.3	+0.1	0.0	+0.2	+0.2	+0.2	+0.2	+0.1	+0.1
Heated with $NaNO_3$ to ignition point of charcoal [h]	−0.5	−0.3	−0.5	−0.5	−0.3	−0.3	−0.5	−0.6	−0.6	−0.4
Heated with $NaNO_3$—Na_2CO_3 mixture for 2 hours: [h]										
After washing	−0.4	−0.3	−0.5	−0.7	−0.7	−0.6	−0.2	−0.5	−0.6	−1.3
After soaking	−0.5	−0.3	−0.5	−0.5	−0.4	−0.4	−0.3	−0.6	−0.5	−1.2
Ignited with Fe_2O_3:										
Before HCl digestion	+0.5	+0.3	+0.5	+0.2	+0.6	+0.5	+0.4	+0.3	+0.3	+0.4
After HCl digestion	−0.1	−0.2	−0.1	−0.2	−0.1	0.0	0.0	0.0	−0.2	−0.1

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[a] The ware withstood this test satisfactorily.

[b] Broke.

[c] Withstood this test without breakage.

[d] Cracked all around on first heat. Recent samples withstood this test.

[e] Fell into two pieces on first heat. Recent samples withstood this test.

[f] Glaze cracked under tongs on first heat.

[g] No cracks developed.

[h] These figures represent the total changes in weight after two or three fusions, respectively, with sodium nitrate.

CONCLUSIONS

In general there is little choice between the five brands of porcelain tested as far as their resistance to reagents is concerned. One exception is their behavior with caustic-soda solution, in which test the Royal Berlin and Japanese wares were the best, if we except the apparently abnormally high result obtained with one of the Berlin dishes.

The two American wares and the Bavarian crucibles made a comparatively poor showing when suddenly heated or cooled. In both of these tests the Japanese and the Royal Berlin porcelain and the Bavarian dishes were equally good. No Berlin crucibles were available.

A serious defect of the American[3] and Bavarian porcelains was the cracking of the glaze when a hot vessel was picked up with tongs.

WASHINGTON, May 18, 1917.

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[3] See footnote 1, p. 3.

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